



Synthesis and electrochemical studies of octahedral nickel β -diketonate complexes

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ABSTRACT

The reaction of $[\text{Ni}(\text{tmhd})_2]$ and $[\text{Ni}(\text{dbm})_2]$ with N-donor chelating ligands in dichloromethane and acetone, respectively, yields the complexes $[\text{Ni}(\text{tmhd})_2(\text{L-L})]$ (L-L = 2,2'-bpy **1**, phen **2** and dmae **3**) and $[\text{Ni}(\text{dbm})_2(\text{L-L})]$ (L-L = 2,2'-bpy **4**, phen **5**, dmae **6**). UV-Vis spectroscopy shows very strong bands in the UV region consistent with ligand centred $\pi \rightarrow \pi^*$ transitions. The electrochemical studies of **1–6** reveal oxidation to Ni(III). The $[\text{Ni}(\text{tmhd})_2(\text{L-L})]$ **1–3** are more easily oxidized by ca. 300 mV and are quasi-reversible whereas for the $[\text{Ni}(\text{dbm})_2(\text{L-L})]$ series only complex **6** shows significant reversibility. X-ray crystallographic studies have been conducted in the case of $[\text{Ni}(\text{dbm})_2(\text{phen})]$ **5** and $[\text{Ni}(\text{dbm})_2(\text{dmae})]$ **6**. The structures both show that the nickel metal centre is octahedral with an O_4N_2 coordination environment. In the structures the β -diketonate ligands exhibit a *cis*-arrangement, with the metal displaced out of the planar chelate ring.

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1. Introduction

Metal β -diketonates, $[\text{M}(\beta\text{-diketonate})_2]$ (β -diketonate = acetylacetonate (acac), hexafluoroacetylacetonate (hfac), 1,3-diphenylpropane-1,3-dione (dbm), 2,2,6,6-tetramethylheptane-3,5-dione (tmhd); M = Mn, Co, Ni, Cu and Zn) have been known for many years and have been extensively studied [1]. These investigations have revealed that in the presence of additional ligands the metal will frequently expand its coordination number from 4 to 6 (Scheme 1) [2]. In the case of divalent nickel this change in coordination number is also accompanied by a spin change from low-spin to high-spin [3].

The resulting adducts have the advantage of additional functionality to tune the metal complexes for a particular application. For instance, simple alkyl diamines (e.g. ethylenediamine) are often used to synthesize volatile precursors suitable for the preparation of metal oxide thin films by chemical vapour deposition [4], while rigid ligands such as imino-pyridines have been used for basic physical studies [3]. More recently, chelating organic radicals have been utilized as ligands for the preparation of single molecule magnets [5–8]. However, despite this wealth of chemistry much of the research still focuses on the acac and hfac ligands with comparatively little research into the more substituted β -diketonate complexes. Furthermore, the redox chemistry of such systems remains

almost completely unexplored [9,10]. Thus, in this paper we report the synthesis, structural and electrochemical characterization of a range of nickel(II) β -diketonate complexes, $[\text{Ni}(\text{tmhd})_2(\text{L-L})]$ and $[\text{Ni}(\text{dbm})_2(\text{L-L})]$ when L-L = 2,2'-bipyridine (2,2'-bpy), 1,10-phenanthroline (phen) and 2-dimethylaminoethylamine (dmae).

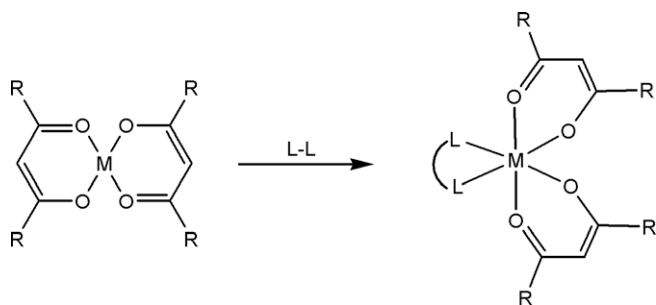
2. Experimental

2.1. General

All reactions were conducted in air using HPLC grade solvents. $[\text{Ni}(\text{tmhd})_2]$ and $[\text{Ni}(\text{dbm})_2]$ were prepared by literature methods [1,11]. Although $[\text{Ni}(\text{tmhd})_2(2,2'\text{-bpy})]$ has been reported previously [2] no explicit synthesis or characterization data was reported and is included for completeness. All other chemicals were purchased from Fluka Chemical Company and used as received. Infrared spectra (as KBr discs) were recorded on a Perkin-Elmer spectrum one infrared spectrophotometer in the range 400–4000 cm^{-1} . Electronic spectra were recorded in CH_2Cl_2 or DMSO on a Unicam UV300 UV-Vis spectrometer. Elemental analyses were carried out on a Eurovector EA3000 analyzer. ESI-MS were carried out on a Bruker Daltonics 7.0 T Apex 4 FTICR Mass Spectrometer. Electrochemical studies were carried out using a palm-sensPC Vs 2.11 potentiostat in conjunction with three electrode cell. The auxiliary electrode was a platinum rod and working electrode was a platinum disc (2.0 mm diameter). The reference was Ag-AgCl electrode. Solution were 5×10^{-4} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte.

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Scheme 1. Formation of $M(\text{acac})_2$ adducts with chelating ligands.

2.2. Synthesis of $[\text{Ni}(\text{tmhd})_2(2,2'\text{-bpy})]$ **1**

$[\text{Ni}(\text{tmhd})_2]$ (0.14 g, 0.30 mmol) was dissolved in dichloromethane (15 ml) giving a pink purple solution and stirred for 10 min. $2,2'\text{-bpy}$ (0.05 g, 0.30 mmol) was added and the solution stirred for 2 h. The resulting green solution was filtered through Celite and evaporated to small volume. *n*-Hexane (10 ml) was added giving a dark green precipitate. The mixture was left at room temperature for 45 min and the green microcrystals collected using a Hirsch funnel and washed with *n*-hexane (5×2 ml), yield 0.14 g (75%). *Anal. Calc.* for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{NiO}_4$: C, 66.1; H, 8.0; N, 4.8. Found: C, 66.2; H, 7.9; N, 5.3%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 397.14 (397.15) $[\text{M}-\text{tmhd}]^+$.

2.3. Synthesis of $[\text{Ni}(\text{tmhd})_2(\text{phen})]$ **2**

$[\text{Ni}(\text{tmhd})_2]$ (0.14 g, 0.30 mmol) was dissolved in dichloromethane (15 ml). The pink-purple solution was stirred for 15 min and then phen (0.06 g, 0.3 mmol) was added, and stirring continued for 1 h. The resulting green solution was filtered through Celite and evaporated to small volume. *n*-Hexane (10 ml) was added and the mixture left at room temperature for 30 min. The resulting green solid was collected using a Hirsch funnel and washed with *n*-hexane (5×2 ml), yield 0.11 g (64%). *Anal. Calc.* for $\text{C}_{34}\text{H}_{46}\text{N}_2\text{NiO}_4$: C, 67.4; H, 7.7; N, 4.6. Found: C, 66.7; H, 7.4; N, 5.2%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 421.14 (421.17) $[\text{M}-\text{tmhd}]^+$.

2.4. Synthesis of $[\text{Ni}(\text{tmhd})_2(\text{dmae})]$ **3**

$[\text{Ni}(\text{tmhd})_2]$ (0.09 g, 0.20 mmol) was dissolved in dichloromethane (15 ml) giving a pink-purple solution and stirred for 10 min. dmae was added (0.02 ml, 0.2 mmol) and the green-blue solution stirred for 1.5 h. The resulting green-blue solution was filtered through Celite and evaporated to small volume. *n*-Hexane (10 ml) was added and the mixture left at room temperature. After 24 h a pastel blue solid appeared, which was isolated by filtration, yield 0.08 g (78%). *Anal. Calc.* for $\text{C}_{26}\text{H}_{50}\text{N}_2\text{NiO}_4$: C, 60.7; H, 9.8; N, 5.5. Found: C, 60.7; H, 9.9; N, 5.8%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 513.31 (513.38) $[\text{M}]^+$, 329.18 (329.12) $[\text{M}-\text{tmhd}]^+$.

2.5. Synthesis of $[\text{Ni}(\text{dbm})_2(2,2'\text{-bpy})]$ **4**

$[\text{Ni}(\text{dbm})_2]$ (0.11 g, 0.20 mmol) was dissolved in acetone (15 ml). The lime green solution was stirred for 15 min and then $2,2'\text{-bpy}$ (0.03 g, 0.20 mmol) was added. The dark green solution was stirred for 2.5 h, filtered through Celite and evaporated to small volume. *n*-Hexane (5 ml) was added, and the solution filtered to give a green solid which was dried in air, yield 0.11 g (89%). *Anal. Calc.* for $\text{C}_{40}\text{H}_{30}\text{N}_2\text{NiO}_4$: C, 72.6; H, 4.6; N, 4.2. Found:

C, 72.7; H, 4.6; N, 4.7%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 437.08 (437.13) $[\text{M}-\text{dbm}]^+$.

2.6. Synthesis of $[\text{Ni}(\text{dbm})_2(\text{phen})]$ **5**

$[\text{Ni}(\text{dbm})_2]$ (0.11 g, 0.20 mmol) was dissolved in acetone (20 ml). The lime green solution was stirred for 15 min and phen (0.02 g, 0.1 mmol) was added. The green solution was stirred for 3.5 h. This resulted in formation of a green precipitate which was collected by filtration and dried in air, yield 0.11 g (80%). *Anal. Calc.* for $\text{C}_{42}\text{H}_{30}\text{N}_2\text{NiO}_4 \cdot 0.2\text{CH}_2\text{Cl}_2$: C, 72.2; H, 4.4; N, 4.0. Found: C, 72.4; H, 4.3; N, 4.3%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 461.08 (461.15) $[\text{M}-\text{dbm}]^+$.

2.7. Synthesis of $[\text{Ni}(\text{dbm})_2(\text{dmae})]$ **6**

$[\text{Ni}(\text{dbm})_2]$ (0.11 g, 0.20 mmol) was dissolved in acetone (15 ml). The lime green solution was stirred for 15 min and then dmae (0.022 ml, 0.20 mmol) was added. The dark green solution was stirred for 3.5 h, filtered through Celite and evaporated to small volume. *n*-Hexane (10 ml) was added and the mixture left at room temperature for 1.5 h resulting in dark green microcrystals isolated by filtration, yield 0.10 g (84%). *Anal. Calc.* for $\text{C}_{34}\text{H}_{34}\text{N}_2\text{NiO}_4$: C, 68.8; H, 5.8; N, 4.7. Found: C, 68.6; H, 5.8; N, 4.7%. Electro spray ionization (ESI) mass data, found (Calc.): m/z 369.11 (369.10) $[\text{M}-\text{dbm}]^+$.

3. Results and discussion

The reaction of $[\text{Ni}(\text{tmhd})_2]$ or $[\text{Ni}(\text{dbm})_2]$ with three chelating ligands, $2,2'\text{-bpy}$, phen and dmae in CH_2Cl_2 or acetone affords green or blue solids of the octahedral complexes $[\text{Ni}(\text{tmhd})_2(\text{L}-\text{L})]$ ($\text{L}-\text{L} = 2,2'\text{-bpy}$ **1**, phen **2** and dmae **3**) and $[\text{Ni}(\text{dbm})_2(\text{L}-\text{L})]$ ($\text{L}-\text{L} = 2,2'\text{-bpy}$ **4**, phen **5** and dmae **6**), see Table 1.

IR spectroscopy of complexes **1–6** shows C—O stretches between 1582 and 1595 cm^{-1} indicating that the β -diketonate ligands adopt a chelating coordination mode [12]. The position of the bands are similar to those reported for $[\text{Ni}(\text{acac})(\text{en})_2]^+$ and $[\text{Ni}(\text{acac})(\text{bpy})_2]^+$ [13]. In addition, the C—H stretches for the tmhd ligand around 2955 cm^{-1} while Ar—H stretches for the dbm ligand are observed between 3055 and 3062 cm^{-1} . Strong bands at around 3364 and 3352 cm^{-1} for **3** and **6**, respectively, are consistent with NH stretches for the amino groups present in these compounds. In all cases the IR spectra are significantly different from the starting materials confirming the presence of the chelating ligand in the metal coordination sphere.

UV–Vis spectroscopy shows very strong bands in the UV region consistent with ligand centred $\pi \rightarrow \pi^*$ transitions. In all cases no d–d transitions were observed presumably due to their low intensity. The NMR spectra of **1–6** are broad and featureless providing little or no structural information and consistent with paramagnetic octahedral Ni(II).

Electrochemical studies conducted in CH_2Cl_2 between ± 1.8 V versus Ag–AgCl electrode at room temperature using a three-electrode configuration reveal one-electron oxidation waves to Ni(III) (Table 2). A representative example of **3** is given in Fig. 1. The waves are quasi-reversible in the case of **1–3**, **6** and irreversible for **4** and **5**. The tmhd complexes are easier to oxidize by ca. 300 mV suggesting that the remote groups on the β -diketonate ligand can significantly affect the electron density on the metal. Interestingly, the bpy and phen ligands show virtually identical peak potentials and are more difficult to oxidize by 110 mV compared with **3** and **6** suggesting that the dmae ligand is a significantly better *net* donor. Further comparisons are somewhat difficult as the only previously reported Ni β -diketonate adducts

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